COATINGS. ENAMELS

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TRANSPARENT VITREOUS COATINGS WITH DECREASED MIGRATION OF BORON AND ALUMINUM IONS INTO ACETIC ACID EXTRACTS

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The results of studying transparent glaze coatings synthesized in the system $Na_2O – K_2O – B_2O_3 – Al_2O_3$ with 12.8 wt.% B_2O, and 3.9 wt.% Al_2O_3 are described. The effect of bivalent modifier cations SrO, MgO, CaO, and their combinations on the physicochemical properties and structure of glass and glass-based coatings is investigated. The optimum composition ranges for glaze coatings that satisfy the standards on the migration of boron and aluminum into food products are identified.

Research into the synthesis of low-melting glaze coatings for ceramics, which could ensure low migration of chemical components in contact with food products, is topical in view of the growing requirements on the quality of ceramics used as food containers. Boron and aluminum are among the elements that are released from transparent glazes and are regulated by sanitary-hygienic standards.

It has been proved that aluminum promotes memory loss and brittleness of bones and impairs mental activity.

Boron is a microelement needed for the normal life activity of organisms. Available data indicate that boron participates in the processes of metabolism of calcium, magnesium, and phosphor and, consequently, is needed to maintain the normal state of bone tissues; however, its daily need humans is not identified.

Thus, the penetration of microelements, in particular, large quantities of boron, which can be accumulated in a human body, and aluminum, which is a toxic element, may lead to serious diseases. The determination of the level of toxic elements released from household ceramics calls for the use of efficient control methods that can protect human health from the danger involved in using dishware that does not meet the hygienic requirements.

According to the sanitary-hygienic standard SanPin 13-3 RB 01, the permissible migration quantity (PMQ) for boron and aluminum released from ceramic ware into a 4% acetic acid solution in 24 h should be not higher than 4 and 0.5 mg/liter, respectively.

The clear glazes currently produced at the factories of the Republic of Belarus are characterized by boron migration within 0.93 – 1.25 mg/liter and aluminum migration within 0.30 – 0.50 mg/liter. Furthermore, the glazes are very sensitive to regime fluctuations in deposition and firing, which may produce slight opalescence on salient areas.

In the European and CIS countries we currently observe the trend of reducing the migration of toxic agents from materials contacting food products. This holds for hygienic standard GN 2.3.3.972.00 adopted in the Russian Federation, which specified a PMQ for boron of not higher than 0.5 mg/liter.

Since boron oxide is classified as danger class 2, same as oxides of lead (its PMQ is 0.03 mg/liter), cadmium (0.001 mg/liter), and arsenic (0.05 mg/liter), the PMQ of 0.5 mg/liter for boron adopted in Russia is quite justifiable. Therefore, to ensure the competitiveness of glazed products on domestic and foreign markets, it is necessary to lower the content of B_2O_3 and, accordingly, decrease its migration from glass glazes and yet have good service parameters. Therefore, we have to develop glaze coatings with a minimum content of the components that may have a negative effect on the human organism.

The purpose of our work is the synthesis of clear vitreous glaze coatings with decreased migration of boron and aluminum ions into food media.

The reference glaze chosen for the development of glaze coatings is glaze No. 189 used at the Belkhudozkeramika JSC (USSR Inventor's Certif. No. 893918) with the following composition, % (here and elsewhere mass content): 68.00 SiO_2, 3.90 Al_2O_3, 17.80 B_2O_3, 8.89 Na_2O, 1.26 K_2O, 0.003 CaO, and 0.12 MgO. This glaze has sufficiently high physicochemical parameters; however, it does not meet the

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European hygienic requirements on the amount of undesirable components released from the coatings, in particular, for boron. Therefore, the composition range selected for our study had a decreased content of B_2O_3, compared with the above composition.

Experimental glasses for clear glaze coatings were melted in porcelain crucibles of capacity 0.3 liters in a gas-flame furnace at $1400 – 1450°C$ with an exposure at the maximal temperature for $1 – 1.5$ h to obtain a homogeneous glass melt without visible batch inclusions in the filament sample. The glasses had good melting and working properties. All glasses retained clarity in frit granulation.

Glaze coatings were prepared by moist milling of frits, adding 7% Vesko-Keramik refractory clay to improve the milling capacity and flow parameters. The moisture of the glaze suspension was $40 – 42\%$. The milling fineness was $0.5 – 0.7\%$ residue on a No. 0063 sieve. The glaze was deposited on majolica articles produced at the Belhudozhkeramika Company that were made of local polymineral clays and subjected to a first firing. The water absorption of molded samples was $20 – 22\%$. The glaze was deposited by the immersion method in the industrial conditions, at 980 and $1000°C$ in the chamber and multichannel electric furnaces of the Belkhudozhkeramika Company.

The content of boron was determined in accordance with GOST 24295–80 by the photometric method based on the reaction of boron with carmine in concentrated sulfuric acid and the formation of tinted complexes. The sensitivity of this method is 0.5 mg/dm^3. The content of aluminum was determined according to GOST 18165–89 by the photometry method as well. The determination of aluminum ions is based on it capacity of forming orange-red lacquer by reacting with colorimetry aluminon in a weakly acid solution at $pH = 4.50 – 4.65$ in the presence of ammonium sulfate; the photometry is performed at the wavelength of $525 – 540$ nm. The aluminum detection limit with confidence probability 0.95 is 0.02 mg/dm^3 for a sample volume of 25 cm^3. The range of measured concentrations is $0.04 – 0.56$ mg/dm^3.

In our studies we identified the range of formation of clear coatings with a decreased content of B_2O_3 based on the high-silica range of the $Na_2O – K_2O – B_2O_3 – Al_2O_3 – SiO_2$ glass-forming system. The content of oxides for the optimum composition range is as follows (%): 10.0 R_2O (9.0 Na_2O, 1.0 K_2O); one of the RO oxides has to be present in the following quantity: $0.03 – 5.00$ CaO, $0.12 – 5.00$ MgO, $0 – 5.00$ SrO. The content of B_2O_3 is within the range of $12.8 – 15.8\%$, Al_2O_3 — $3.9 – 7.0\%$, the rest is SiO_2. The following combinations of RO oxides are possible as well (%): $0.8 – 3.8$ CaO and $0.6 – 2.1$ MgO; $0.6 – 2.9$ CaO and $0.6 – 1.5$ SrO while maintaining the above specified quantities of Na_2O, K_2O, Al_2O_3, and B_2O_3. In this case the two-charge oxide cations (calcium, magnesium, strontium) and their combinations were introduced into glazes instead of boron oxide.

The microhardness of the glaze coatings was determined on a PTM-3M instrument (the LOMO Company, Russia) under a 100 g load on the indenter, and the data were processed using a photoelectron micrometer (Spektr Company, Russia). The determination error is $\pm 2 – 3\%$.

The experiment established that the microhardness of glaze coatings varies from 5400 to 7500 MPa; the microhardness of glaze coatings containing 12.8% B_2O_3 is higher than in coatings containing 15.8% B_2O_3. This is probably due to the preservation of three-coordination boron in the system, which decreases the total cohesion of the alumino-borosilicate skeleton and, accordingly, reduces the microhardness.

The CLTE and the softening temperature of the synthesized glaze glasses were measured on a DIL 402 PC electron dilatometer produced by Netzsch (Germany) in the temperature interval of $200 – 800°C$ at a constant heating rate of samples in the furnace equal to 5 K/min.

The experimental CLTEs of the studied glaze glasses are $(55.1 – 62.2) \times 10^{-7}$ K^{-1}. An increase in the quantity of B_2O_3 from 12.8 to 15.8% decreases the CLTE. The experimental determination of the CLTE in clear calcium-, magnesium-, and strontium-bearing glasses indicates that an increase in the content of CaO, MgO, and SrO raises the CLTE. It is known that the CLTE depends mainly on the strength of bonds between structural elements, their reaction capacity, and packing density. A decrease in the specified structural parameters increases the CLTE of the glasses. The calculated CLTE values are $1 – 2\%$ higher than the experimental values.

It is found that the softening temperature of the considered glasses varies from 640 to 590°C; it grows with an increasing SiO_2 content and decreases with a growing B_2O_3 content, which directly depends on the strength of bonds between the ions. It should be noted that the softening point of calcium and strontium-bearing glasses is somewhat higher than that of magnesium-bearing glasses. An increase in CaO and CrO content from 1 to 5% leads to an insignificant decrease in the softening temperature, whereas introduction of magnesium oxide raises this temperature.

Analyzing the quantity of boron released into 4% acetic acid solution from the glaze coatings with the content of boron equal to 12.8 and 15.8% and the fusion temperature of 980 and 1000°C, we can see that it does not exceed the maximum permissible quantity (0.5 mg/liter).

As for the migration of aluminum ions, for the compositions that do not contain bivalent cations at temperatures of 980 and 1000°C it is equal on the average to 0.50 mg/liter, which corresponds to the admissible migration quantity. For all other compositions containing $3.9 – 7.0\%$ Al_2O_3, the concentration of aluminum ions released into the 4% solution of acetic acid is equal to $0.02 – 0.33$ mg/liter, which is below the PMQ.

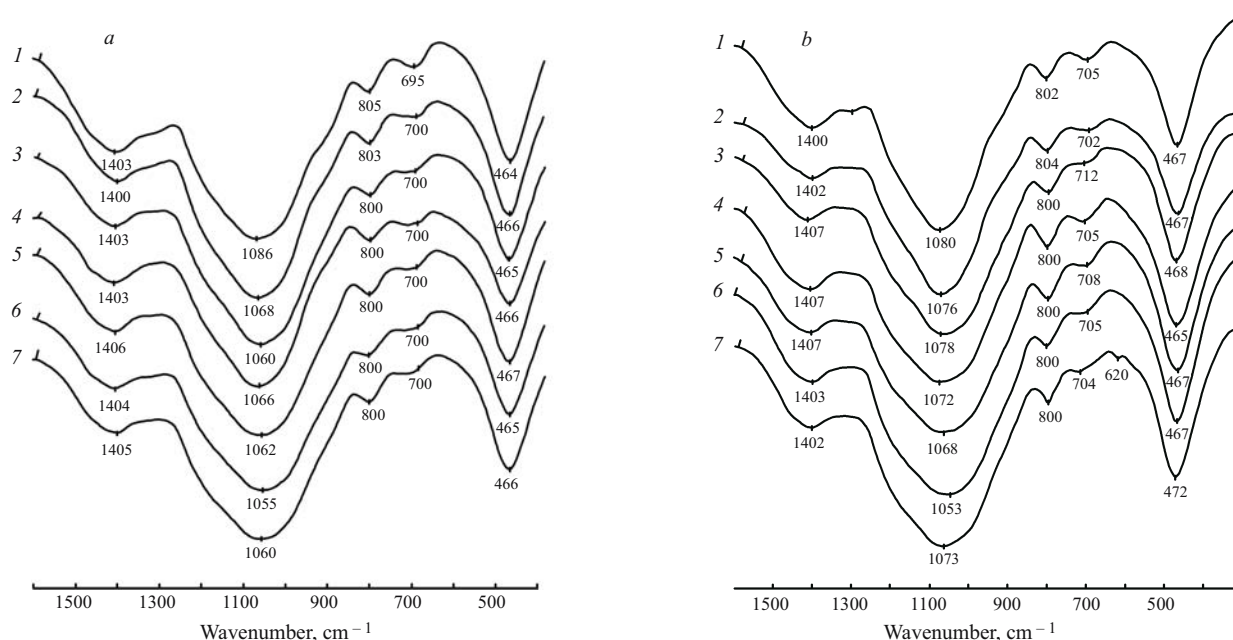The optimal compositions containing calcium, magnesium, and strontium oxides and their combination release

Fig. 1. IR absorption spectra of initial (*a*) and heat-treated at 980°C (*b*) glasses of the $Na_2O - K_2O - RO - B_2O_3 - Al_2O_3 - SiO_2$ system with the constant content of 3.9% Al_2O_3 and 12.8% B_2O_3. Curve numbers correspond to compositions numbers: *1*) without RO, 15.8 % B_2O_3; *2*) without RO; *3*) 5% CaO; *4*) 5% MgO; *5*) 3.75% CaO + 1.25% MgO; *6*) 5% SrO; *7*) 2.5% CaO + 2.5% SrO.

fewer aluminum ions into the model medium than the composition without two-charge cations. This is probably due to the fact that the specified oxides facilitate the transition of aluminum into the four-coordination state, which strengthens the aluminoborosilicate skeleton.

Thus, the synthesized compositions meet the European standard requirements regarding the migration of aluminum and boron into model acetic acid extracts.

Since the structural state of boron in a glass has a significant effect on its properties, we performed IR-spectroscopic analysis of the initial glasses and glasses heat-treated at 980°C to determine the degree of their inhomogeneity as well as the presence of structural groups.

The characteristic feature of the considered system of glaze glasses is the fact that its three cations (B^{3+}, Al^{3+}, Si^{4+}) are capable of participating in the formation of the structural glass lattice. At the same time, cations B^{3+} and Al_3 may change their oxygen coordination number depending on the ratio between the particular oxides in glass and, consequently, significantly affect the structure and properties of glass.

Figure 1*a* shows the IR absorption spectra of glasses with different contents of RO and a constant sum of the alkali oxides equal to 10%. The IR spectra were obtained on a NEXUS spectrophotometer produced by the NICOLET Company (USA). The samples were prepared by compressing a mixture of KBr powder and the material analyzed (300 : 1).

The initial glass spectra exhibit absorption bands in the range of 1400, 1055 – 1068, 800, 700, and 465 cm^{-1}. The main absorption band is observed at 1055 – 1068 cm^{-1},

which suggests the existence of ranges with actually undisturbed Si – O – Si bonds. The certain shift of the main band maximum toward the low-frequency range in the glass spectra may be a consequence of the isomorphic substitution of aluminum ions for a part of the silicon ions in the silicon-oxygen tetrahedrons. The vibrations of atoms in the Si – O – Si bonds also correlate with the absorption bands at 680 – 720 and 400 – 500 cm^{-1}. The absorption band in the range of 800 cm^{-1} points [1] to the possibility of the presence of hexad rings from the tetrahedrons [SiO_4] in the glass skeleton.

The absorption bands with maxima at 720, 790, and 810 cm^{-1} can be caused [1] by splitting triply degenerate atom vibrations in [AlO_4] groups.

According to A. A. Appens's data [2], when the function of the molar ratio $\Psi_B = (R_2O + RO) - Al_2O_3]/B_2O_3$ ranges from 1/3 to 1, boron ions exist in two coordination states, i.e., [BO_3] and [BO_4]. The absorption band with the maximum at 1400 cm^{-1} [1] belongs to the asymmetric twice degenerate stretching vibrations of atoms the B – O bonds and the [BO_3] triangle. The intensity of the absorption band with the maximum around 1400 cm^{-1} in the considered glass decreases upon the transition from magnesium- and calcium-bearing glasses to strontium-bearing ones.

This is apparently due to the fact that not all oxygen introduced via the RO, but only its active part, influences the coordination state of boron in glass. RO oxides "give up" their oxygen to boron not as easily. Small-radius cations with an intense force field retain oxygen stronger than cations with a large radius. In the glass containing magnesium oxide

($r = 0.074$ nm) [2], a partial incorporation of boron into the silicon-oxygen skeleton occurs only due to the oxygen introduced by the oxides of alkali metals. As for CaO ($r = 0.104$ nm) and SrO ($r = 0.120$ nm), they can more or less intensely influence the state of B_2O_3 in glass. Since the content of B_2O_3 is constant, this uniquely proves the change in the ratio between the groups $[BO_3]$ and $[BO_4]$ due to the transition of boron from three coordination to four coordination. This is also corroborated by the decreased intensity of the absorption band in the range of 700 cm^{-1}. This absorption band corresponds to three-coordination boron and reflects the extraplanar deformation vibrations of B(III) – O – B(III) bonds [1].

Thus, according to the IR spectroscopy data, the modifier cations affect the coordination transformation $[BO_3] – [BO_4]$. The larger the ionic radius, the smaller is the absorption band corresponding to three-coordination boron.

Thermal treatment of glasses at 980°C does not perceptibly change the IR spectra. We observe just a slight increase in the degree of polymerization of the main structural groups (Fig. 1b). The main band maximum in this case shifts from 1053 to 1080 cm^{-1}. This is due to the increased degree of polymerization of the aluminosilicon-oxygen groups and the transition from laminar and chain groups to skeletal ones [1]. The narrowed absorption bands in all other spectrum ranges indicate an ordering of structural groups in the aluminoborosilicate skeleton.

The specific structure of glasses and glass-based coatings modified by alkali oxides is due to the incomplete transformation of groups $[BO_3]$ into groups $[BO_4]$, although the total quantity of metal oxides (R_2O and RO types) that are oxygen donors is sufficient for a complete transition of boron into four coordination. This is probably responsible for the migration of boron ions to the acetic acid solution, since three-coordination boron is less resistant to it. As for Al_2O_3, its introduction within the entire interval of 3.9 – 7.0% leads to the preservation of tetrahedral groups $[AlO_4]$, which ensures the migration of aluminum ions satisfying the standard.

The obtained results agree well with A. A. Appen's conclusions [2] that the main factor responsible for the coordination state of cations is the degree of acidity-basicity of glass. Ions Si^{4+} can be replaced by ions Al_3 and B_3 that have crystal-chemical similarity with them; in that case an integrated "mixed" skeleton" may be formed. According to A. A. Appen [2], the structural state of cations Al^{3+} and B^{3+} coexisting in glass primarily depends on the ratio Ψ_B. Calculation of this ratio indicates that the glass structure should contain groups $[AlO_4]$, $[BO_4]$, and $[BO_3]$. The calculation results agree well with experimental data.

Analysis of the glaze glass structure by electron microscopy identified the presence of liquation in the initial glasses and in glaze coatings based on them. The microinhomogeneities have the form of clearly defined or blurred drops. The results of x-ray phase analysis show that all the
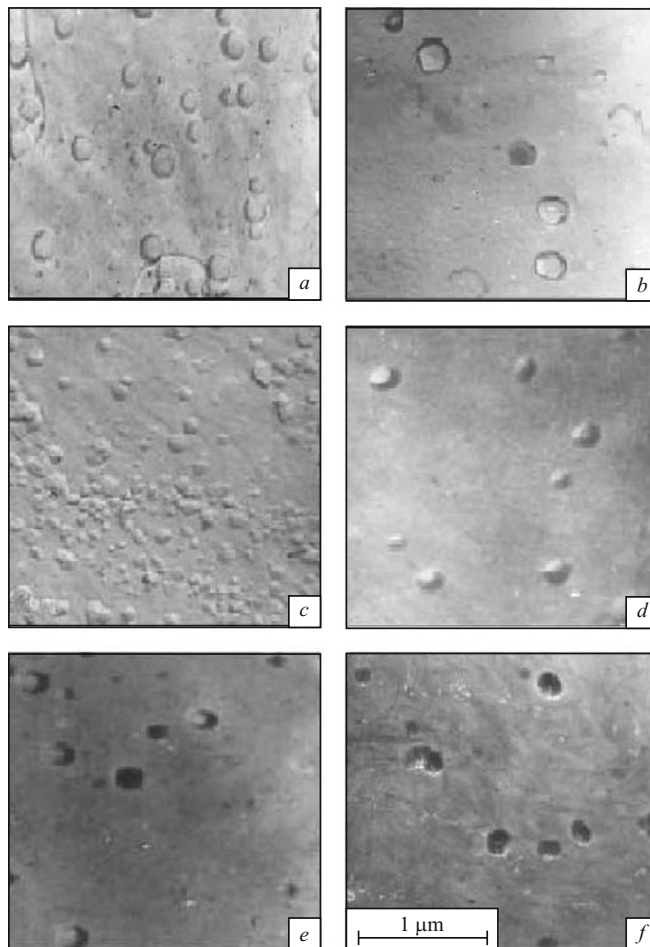

Fig. 2. Electron microscope photos of glaze coatings heat-treated at 980°C with the constant content of 3.9% Al_2O and 12.8% B_2O_3: $a – f$) compositions 2 – 7, respectively.

considered glasses are x-ray-amorphous. The electron microscope photos of the glaze coatings are shown in Fig. 2.

Based on electron microscopy data, the glaze coating not containing oxides of bivalent metals exhibits drop liquation with a drop size of 0.1 – 0.3 μm, which leads to phase separation. The compositions containing CaO, MgO, and SrO, each in the amount of 5%, upon exposure at 980°C exhibit the homogenization of the melt; consequently, the coating in fact has a single phase.

The glaze coatings containing 3.75% CaO and 1.25% MgO, as well as 2.50% CaO and 2.50% SrO after firing at 980°C and a 60 min exposure exhibit liquation drops of size 0.1 – 0.2 μm. The minimum propensity for liquation separation is registered in the strontium-bearing glaze coating.

The tendency to phase separation agrees well with the known postulate on liquation growing with growing intensity of the modifier ion field [2]. In this case $Sr^{2+} \rightarrow Ca^{2+} \rightarrow Mg^{2+}$. Phase separation in the considered system is caused by the incompatibility of silicon-oxygen tetrahedrons with boron-oxygen triangles, whereas the presence of a small quantity of an alkaline-earth oxide just reveals this immiscibility.

Analyzing the data of electron microscopy of glaze coatings, one can see that boron oxide in the three-coordination state is responsible for the development of liquid processes in glass.

The experiment performed has demonstrated that steady transparent coatings can be obtained by controlling the mechanism of formation of single-phase glazes in the $BaO – B_2O_3 – Al_2O_3 – SiO_2$ glass-forming system by introducing RO modifier oxides (CaO, MgO, SrO, and their combinations) instead of boric anhydride. Moreover, the limiting concentration of Al_2O_3 introduced instead of SiO_2 has been determined.

The homogenizing role of Al_2O_3 in glasses and glaze coatings has been confirmed. Its optimum quantity ensuring that migration of aluminum ions is below the prescribed DMQ standard should be 3.9 – 7.0%. The currently accepted theory of the homogenizing effect of Al_2O_3 due to the formation of $[AlO_{4/2}]R$ complexes [3] provides a sufficiently complete explanation for the formation of a monophase or a nearly monophase structure in the considered glasses and coatings. The structure of clear glasses and coatings typically has an aluminosilicon-oxygen skeleton formed by tetrahedral elements $[SiO_4]$, $[AlO_4]Na$, and $[BO_4]Na$.

The compliance of toxic concentrations with permissible levels was the main criterion in estimating the quality of ceramic glaze coating intended for contact with food products. It is experimentally established that as boric anhydride content in the developed glass compositions decreases, its migration into the acetic acid extract decreases as well and is below 0.5 mg/liter, which satisfies the international sanitary standard. The optimum content of B_2O_3 is 12.8 – 15.8%. The migration of aluminum ions into the acetic acid extract does not exceed the maximum permissible concentrations either. Consequently, the proposed glaze coatings can be used for food containers.

The developed glazes satisfy the required level of physicochemical properties. Their application provides savings by decreasing the use of expensive boron-bearing materials.

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